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Final Technical Report
Ultrafast Dynamics of Condensed Phase Systems
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Craig C. Martens

Department of Chemistry

University of California, Irvine

Irvine, CA 92697-2025

949-824-8768

949-824-8571 FAX

cmartens@uci.edu

Abstract

In this final report, we describe the results of our ONR-funded research project in theoretical and computational chemistry. We briefly review our ONR-supported work in the following areas: (1) Development of methodology for simulating nonadiabatic dynamics in molecular systems. (2) A proposal for a new type of direct spectroscopy of ultrafast many-body bath dynamics, called nanoscale shock wave spectroscopy, and the results of molecular dynamics simulations describing its theoretical implementation.

The general goal of our ONR-sponsored research in theoretical and computational chemistry has been the understanding of ultrafast dynamics in many-body systems. The mechanical processes occurring in matter on length scales measured in nanometers and time scales measured in femtoseconds ultimately dictate its bulk chemical and physical properties. The details of these elementary processes are far from being completely understood. Fortunately, modern experimental techniques are creating an ever-widening window into these regimes. Ultrafast laser pulse technology makes possible the real time interrogation and observation of the actual motions of

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atoms and electrons occurring with characteristic time scales of as short as 10^{-15} s, and provides opportunities and challenges for theory.

During the period covered by this report, our work has been concerned with both methodological developments and their application to the study of ultrafast phenomenology. Our recent emphasis has been on methodology, most notably the introduction and development of a new approach to modeling nonadiabatic processes in the context of classical mechanical molecular dynamics simulations. The method has been well received, and we believe that it constitutes a significant advance. We briefly summarize our recent work here. Further information can be found in our annual reports, publications, and preprints.

• **Semiclassical-limit nonadiabatic molecular dynamics**

In this project, we have developed a new approach for treating nonadiabatic dynamics in molecular systems, based on a semiclassical limit of the quantum Liouville equation describing nuclear (i.e., vibrational) dynamics on coupled electronic surfaces. [1-3] By employing a semiclassical expansion of the quantum Liouville equation, we derived equations of motion resembling a generalized nonequilibrium statistical mechanics of the state populations, and notably, the off-diagonal coherences between the electronic states. We then exploited this representation to devise a numerical implementation in terms of classical trajectories and ensemble averaging. [2-4] Unlike other classical trajectory-based approaches, such as Tully's surface hopping algorithm, the electronic coherence is treated in a rigorous manner by our Liouville-based method. This has allowed our classical trajectory approach to be applied to manifestly coherent processes, such as our recently proposed "nonadiabatic wavepacket interferometry" ultrafast experiment. [5]

• **Nanoscale shock wave spectroscopy: a direct view of ultrafast bath dynamics**

This work constitutes a first step in our general effort to develop "bath spectroscopies"—theoretical but realizable spectroscopies which allow nontrivial many-body processes in solvents and host materials to be viewed directly. We recently

initiated a study that focuses on observable signatures of the generation, propagation, and decay of nanoscale shock waves. These are highly localized supersonic atomic disturbances can be generated in hosts by highly energetic dynamics in impurities excited by femtosecond laser pulses.[6] We performed molecular dynamics simulations on a model system and synthesized pump-probe signals using our previously developed numerical methods.[7] The key difference between existing pump-probe measurements and our newly devised scheme is that the probe laser is absorbed by the host itself, rather than by the chromophore impurity. In particular, the probe laser interacts with atomic scale regions that are localized within the travelling shock front, while unperturbed regions remain transparent. This allows the nanoshock process to be observed.[8]

ONR-supported publications cited

[1]   C. C. Martens and J.-Y. Fang, *J. Chem. Phys.* **106**, 4918-30 (1997).

[2]   A. Donoso and C. C. Martens, *J. Phys. Chem.* **102**, 4291 (1998).

[3]   A. Donoso and C. C. Martens, in *Laser Techniques for Condensed-Phase and Biological Systems*, Vol. 3273, edited by N. F. Scherer and J. M. Hicks (SPIE, 1998), pp. 10.

[4]   A. Donoso and C. C. Martens, *Mexican J. Phys.*, (2000).

[5]   A. Donoso, D. Kohen, and C. C. Martens, *J. Chem. Phys.* **112**, 7345 (2000).

[6]   A. Borrmann and C. C. Martens, *J. Chem. Phys.* **102**, 1905-16 (1995).

[7]   Z. Li, J. Y. Fang, and C. C. Martens, *J. Chem. Phys.* **104** (1996).

[8]   D. Kohen and C. C. Martens, *J. Chem. Phys.* **111**, 4343 (2000).